

# Large oxygen-isotope shift above the quantum critical point of $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$

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We have studied the oxygen-isotope effect on the superconducting transition temperature  $T_c$  in overdoped  $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  with  $x = 0.10, 0.20$ , and  $0.25$ . We find the oxygen-isotope exponent  $\alpha_O$  to be small ( $\sim 0.02$ ) for  $x = 0.10$  but substantial ( $\sim 0.1$ ) for  $x = 0.20$  and  $0.25$ . The doping level above which  $\alpha_O$  increases sharply coincides with a quantum critical point where the normal-state pseudogap starts to diminish. The present isotope-effect experiments provide direct and quantitative constraints on the pairing mechanism of high-temperature superconductivity in cuprates.

The importance of phonons in the pairing mechanism can usually be checked by the dependence of  $T_c$  on the isotope-mass  $M$  (isotope effect). For most conventional phonon-mediated superconductors, the isotope exponent ( $\alpha = -d \ln T_c / d \ln M$ ) is close to 0.5, as expected from the BCS theory. For high- $T_c$  cuprate superconductors, the isotope effects have been investigated by several groups with consistent results [1, 2, 3, 4, 5, 6, 7]. There are small oxygen- and copper-isotope exponents in optimally-doped cuprates, but large exponents (even larger than 0.5) in underdoped cuprates [8]. Due to the high  $T_c$  values and the earlier observation of a very small oxygen-isotope exponent ( $\alpha_O \simeq 0.02$ ) in an optimally-doped cuprate superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  (YBCO) [1, 2, 3], most researchers believe that electron-phonon coupling cannot be the origin of 90 K superconductivity in YBCO. On the other hand, it is extremely difficult to understand the large  $\alpha_O$  and the substantial oxygen-isotope effect on the in-plane supercarrier mass ( $m_{ab}^*$ ) in underdoped cuprates [8, 9, 10] if the electron-phonon interactions were not strong. The large oxygen-isotope effects on both  $T_c$  and  $m_{ab}^*$  in underdoped cuprates can be consistently explained if one considers that  $T_c$  in underdoped cuprates is essentially proportional to  $n_s/m_{ab}^*$  (where  $n_s$  is the supercarrier density) [11] due to a Bose-Einstein-like superconducting transition and that  $m_{ab}^*$  depends on the isotope mass due to a polaronic effect [12]. For optimally-doped YBCO where the superconducting transition is mean-field-like, the small  $\alpha_O$  and substantial oxygen-isotope effect on  $m_{ab}^*$  [13, 14, 15] can be consistently explained by a scenario where polarons are bound into the Cooper pairs [14].

Now a question arises: What happens to  $\alpha_O$  when the polaronic effect disappears? Electronic specific-heat data indicate that there exists a quantum critical point at a doping level  $p_{cr}$  of about 0.19 in YBCO and Ca substituted YBCO, above which the normal-state pseudogap disappears [16]. For  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (LSCO), the normal-state pseudogap state is still present up to a doping level of 0.24 (Ref. [16]), implying that  $p_{cr} > 0.24$  in this system. Although the origin of the normal-state pseudogap is still debated, one plausible explanation is that there co-exist Fermi-liquid-like carriers and polaronic/bipolaronic oxygen holes and that the pseudogap is related to the bipolaron binding energy [17]. Above the quantum crit-

ical point, the pseudogap diminishes along with the disappearance of polaronic and bipolaronic oxygen-holes so that the superconducting transition becomes more conventional. If the superconducting pairing is mainly mediated by phonons, the isotope effect on  $T_c$  should become large above the quantum critical point. Therefore, above this critical point, the recovery of the large conventional isotope exponent would unambiguously expose electron-phonon coupling as an important pairing mechanism.

Here we report studies of the oxygen-isotope effect on the superconducting transition temperature  $T_c$  in overdoped  $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  with  $x = 0.10, 0.20$ , and  $0.25$ . We find that the oxygen-isotope exponent  $\alpha_O$  is small ( $\sim 0.024$ ) for  $x = 0.10$  and becomes substantial ( $\sim 0.1$ ) for  $x = 0.20$  and  $0.25$ . The doping level above which  $\alpha_O$  increases sharply appears to coincide with the quantum critical point where the normal-state pseudogap starts to diminish. We further show that a combined mechanism based on strong coupling to multiple phonon modes and significant coupling to high-energy (1.6-2.0 eV) charge fluctuations is in quantitative agreement with the oxygen-isotope exponent and magnetic penetration depth above the quantum critical point as well as with thermal-difference reflectance data.

Samples of  $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  were prepared by a conventional solid-state reaction using  $\text{CaCO}_3$  (99.99%),  $\text{BaCO}_3$  (99.997%),  $\text{CuO}$  (99.995 %), and  $\text{Y}_2\text{O}_3$  (99.999 %). The powders were mixed, ground thoroughly, and fired in air at 950 °C for  $\sim 24$  hours with one intermediate grinding. The samples were ground again, pressed into pellets, and sintered in air at 920 °C for  $\sim 20$  hours. To obtain samples with small grains and sufficient porosity for the isotope experiments, we reground the samples thoroughly, pressed them into pellets, and annealed them in air at 800 °C for 20 hours.

Three pairs of the samples with different Ca concentrations were wrapped in gold foil and subjected to  $^{16}\text{O}$  and  $^{18}\text{O}$  isotope diffusion. The diffusion was carried out for about 48 hours at 750 °C and in an oxygen partial pressure of about 0.8 bar with one intermediate refilling of the isotope gases. The cooling rate from 750 °C to 670 °C is about 1.7 °C/minute, and the average cooling rate from 670 °C to 350 °C is about 10 °C/minute. The oxygen isotope-enrichment was determined from the weight change of the  $^{18}\text{O}$  sample. The  $^{18}\text{O}$  samples were thus

found to have  $\sim 96\%$   $^{18}\text{O}$  and  $\sim 4\%$   $^{16}\text{O}$ .

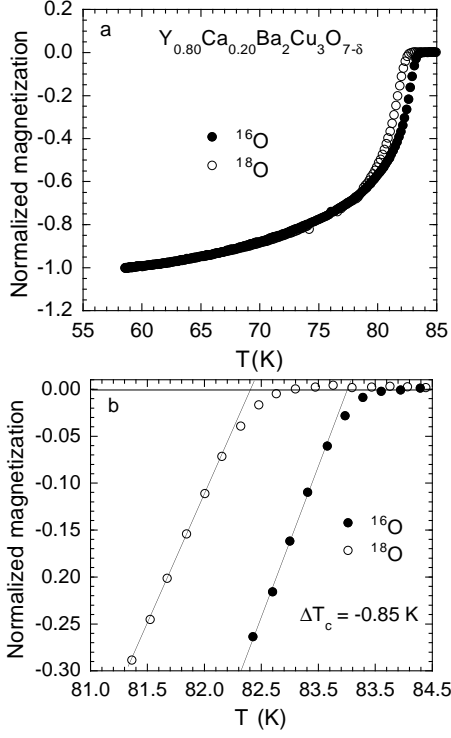


FIG. 1: a) Temperature dependencies of the normalized magnetizations for the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples of  $\text{Y}_{0.80}\text{Ca}_{0.20}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ . b) The expanded view near the transition region. The oxygen-isotope shift is  $0.85 \pm 0.04$  K.

Magnetization was measured with a Quantum Design sample vibrating magnetometer (VSM). The Meissner effect was measured in a magnetic field of 1 Oe or 10 Oe after the samples had been cooled from the normal state in the field. Data were taken continuously during cooling and warming with a same rate. For most measurements, the cooling and warming rates are 1 K per minute. Such slow cooling and warming rates ensure a very small thermal lag, which is about 0.5 K. Increasing the rate to 3 K per minute increases the thermal lag to about 1.5 K, but the isotope shift is nearly independent of the rate. The data in Fig. 1 and Fig. 2 below are corrected for these thermal lags.

Figure 1a show temperature dependencies of the normalized magnetizations for the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples of  $\text{Y}_{0.80}\text{Ca}_{0.20}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ . It is apparent that the magnetizations of the two isotope samples show a parallel shift. In order to see the isotope shift more clearly, we show in Fig. 1b the expanded view near the transition region. We clearly see that the  $T_c$  of the  $^{18}\text{O}$  sample is significantly lower than that of the  $^{16}\text{O}$  sample. If the transition temperature is determined from the linear portion of the magnetization data extended to the base line as indicated in the figure, we find that the isotope shift is 0.85 K. The oxygen-isotope exponent  $\alpha_O = -d \ln T_c / d \ln M_O$  is calculated to be 0.092, which is larger than the Sn isotope

exponent (0.08) in the conventional phonon-mediated superconductor  $\text{Nb}_3\text{Sn}$ . In contrast, the isotope shift in  $\text{Y}_{0.90}\text{Ca}_{0.10}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  is significantly smaller, as seen in Fig. 2. The oxygen-isotope exponent is calculated to be 0.024. The magnitude of the isotope exponent for  $\text{Y}_{0.90}\text{Ca}_{0.10}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  is very close to that (0.027) for optimally doped  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (Ref. [13]).

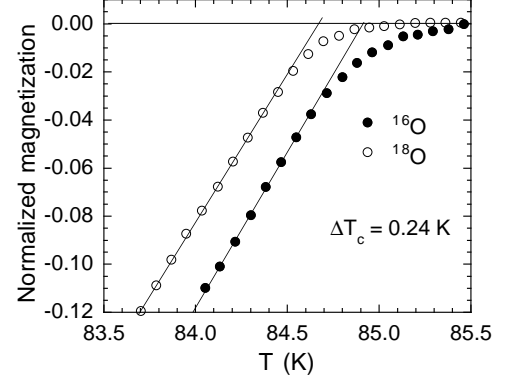


FIG. 2: a) Temperature dependencies of the normalized magnetizations for the  $^{16}\text{O}$  and  $^{18}\text{O}$  samples of  $\text{Y}_{0.90}\text{Ca}_{0.10}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ . The oxygen-isotope shift is  $0.24 \pm 0.04$  K.

In Figure 3, we plot  $\alpha_O$  and  $T_c$  as a function of Ca content  $x$ . The data for  $x = 0$  are taken from Ref. [13]. It is striking that the isotope exponent remains constant and small for  $x$  between 0 and 0.10, and jumps to large values (about 0.1) for  $x = 0.20$  and 0.25. We will show that this unusual doping dependence is associated with a quantum critical point at a critical doping level of about 0.19.

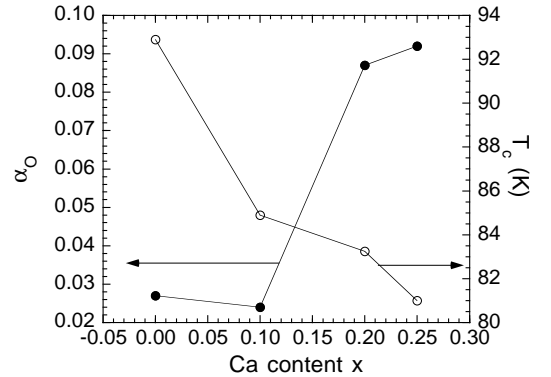


FIG. 3: The oxygen-isotope exponent  $\alpha_O$  and  $T_c$  as a function of Ca content  $x$  in  $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ . The data for  $x = 0$  are taken from Ref. [13].

The oxygen content of our samples can be estimated from the final cooling rate we use to prepare the samples. Studies of the effect of the cooling rate on the oxygen content in ceramic samples of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  indicate that the oxygen content at a cooling rate of 10  $^\circ\text{C}/\text{minute}$  has no difference from that at a cooling rate of 1  $^\circ\text{C}/\text{minute}$ .

It is also established [19] that the  $\delta$  value is about 0.07-0.08 for ceramic samples cooled in 1 bar oxygen partial pressure and at a cooling rate of about 1 °C/minute. Therefore, the  $\delta$  value of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  should be about 0.1 when it is cooled in 0.8 bar oxygen partial pressure and at the cooling rate of 10 °C/minute. It is also shown [20] that Ca substitution does not change the average Cu valence so that  $\delta = \delta_0 + x/2$ , where  $\delta_0$  is the concentration of the oxygen vacancies for  $x = 0$ . The bond-valence sum calculations (see Fig. 4 of Ref. [21]) indicate that the oxygen vacancies do not equally reduce the hole doping levels of  $\text{CuO}_2$  planes and  $\text{CuO}$  chains while Ca substitution contributes holes mainly to  $\text{CuO}_2$  planes. Therefore, Ca substitution leads to overdoping of  $\text{CuO}_2$  planes and underdoping of  $\text{CuO}$  chains to keep the same average Cu valence. With  $\delta_0 = 0.1$  estimated from our preparation conditions, we find the  $\delta$  values of our Ca substituted samples to be 0.15, 0.20, and 0.225 for  $x = 0.10, 0.20$ , and 0.25, respectively.

Figure 4 shows the  $\delta$  values of our Ca substituted samples as a function of  $x$  together with the  $\delta_{OP}$  values corresponding to the optimal  $T_c$ 's with  $p = 0.16$ . It is apparent that the difference between  $\delta_{OP}$  and  $\delta$  becomes more pronounced above  $x = 0.13$ . We can estimate the hole doping level  $p$  of  $\text{CuO}_2$  planes from the bond-valence sum calculations which show that  $dp/d\delta = -0.20$  for  $\delta < 0.5$ . Using  $dp/d\delta = -0.20$  and the difference  $\delta_{OP} - \delta$  (see Fig. 4), we calculate the  $p$  values to be 0.18 and 0.21 for  $x = 0.10$  and 0.20, respectively. With  $p_{cr} = 0.19$  for the double-layer cuprates, one can see that the  $x = 0.10$  sample is below the quantum critical point and the  $x = 0.20$  sample is above it.

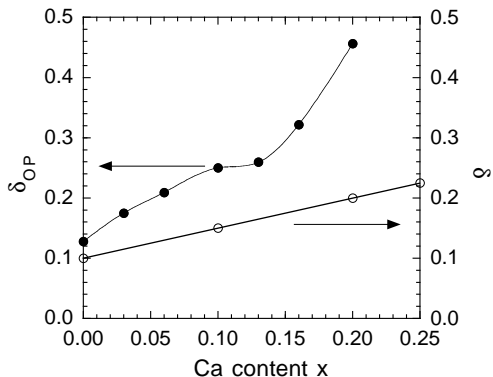


FIG. 4: The concentration  $\delta$  of oxygen vacancies in  $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  as a function of  $x$  together with the  $\delta_{OP}$  values corresponding to the optimal  $T_c$ 's with  $p = 0.16$ . The  $\delta_{OP}$  data are from Ref. [21].

If the normal-state pseudogap is associated with local pairs of polaronic oxygen holes, the sudden increase of the oxygen-isotope exponent just above the quantum critical point, where the normal-state pseudogap diminishes, is consistent with the disappearance of polaronic oxygen holes. Diminishing polaronic effect above  $p_{cr}$  makes the

superconducting transition more conventional so that the total isotope exponent will be close to 0.5 if electron-phonon coupling mainly contributes to the electron pairing. The fact that the observed oxygen-isotope exponent above  $p_{cr}$  is substantial (about 0.1), but still significantly below 0.5, implies that other non-oxygen related phonon modes and/or high-energy electronic bosonic modes also contribute to the electron pairing. On the assumption that the electron-phonon spectral function  $\alpha^2(\omega)F(\omega)$  is simply proportional to the phonon density of states measured by neutron inelastic scattering, Rammar [22] calculated the oxygen-isotope exponent to be 0.08-0.10 for an electron-phonon coupling constant  $\lambda_{e-ph}$  in the range of 1.4 to 6.5 and effective Coulomb pseudopotential  $\mu_{eff}^*$  in the range of  $-0.15$  to  $0.30$ . A negative  $\mu_{eff}^*$  value is required to obtain 91 K superconductivity for smaller  $\lambda_{e-ph}$ . For example,  $\mu_{eff}^* = -0.15$  when  $\lambda_{e-ph} = 1.4$ . Within the combined phonon and nonphonon mechanism, the negative  $\mu_{eff}^* = \mu^* - \lambda_{e-el}$  (Ref. [23]) is possible only when the coupling constant  $\lambda_{e-el}$  of high-energy electronic bosonic modes is larger than the Coulomb pseudopotential  $\mu^*$ , which has a typical value of 0.10-0.15 for most conventional superconductors. Our measured  $\alpha_O$  is in quantitative agreement with the calculated values (0.08-0.10) that are nearly independent of the  $\mu_{eff}^*$  values. Furthermore, the simple assumption of the multiple-phonon coupling made by Rammar [22] is consistent with tunneling and angle-resolved photoemission spectra, which show multiple-phonon coupling features that precisely match with the peak features in the phonon density of states [24].

The relative contribution of electron-phonon coupling in superconducting pairing depends on the average electron-phonon coupling constant. The tunneling spectrum [25] of optimally doped  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$  indicates that the electron-phonon coupling constant is about 3. Since this tunneling spectrum may mainly probe the anti-nodal states that have the maximum coupling constant, the average coupling constant over the entire Fermi surface should be approximately 1.5 (the half of the maximum value) due to extended- $s$  wave gap symmetry with eight line nodes [26, 27]. For the fully oxygenated  $\text{YBa}_2\text{Cu}_3\text{O}_7$  with  $T_c = 89$  K, the doping level  $p$  is just at the critical point [16], suggesting negligible polaronic effect. The in-plane penetration depth for this compound [28] is found to be  $103 \pm 8$  nm, corresponding to an effective plasma energy of  $1.92 \pm 0.14$  eV. With a bare in-plane plasma energy of 2.9 eV (Ref. [29]), we find that the masses of charge carriers are enhanced by a factor of  $2.28 \pm 0.35$ , implying that the average  $\lambda_{e-ph}$  is  $1.28 \pm 0.35$ . With  $\lambda_{e-ph} = 1.3$ , it is required to have  $\mu_{eff}^* = -0.16$  to obtain 89 K superconductivity. Indeed, thermal-difference reflectance data of several cuprates show that [30] the coupling constant to high-energy (1.6-2.0 eV) charge fluctuations is in the range of 0.25-0.30. This implies that  $\mu_{eff}^*$  should be in the range of  $-0.10$  to  $-0.20$  with  $\mu^* = 0.10$ -0.15. Therefore, the strong inter-

actions of electrons with both phonons and charge fluctuations can cause 90 K superconductivity.

Now we discuss the origin of the quantum critical point. It is well known that undoped parent compounds are charge-transfer insulators due to strong electron-electron correlation. Therefore, doped holes mainly reside on the oxygen orbitals as long as the charge-transfer gap is larger than a critical value. The doped oxygen holes can form polarons and bipolarons due to strong electron-phonon interactions [12]. For LSCO, this should happen for  $p < 0.10$  (Ref. [17]). When the doping level increases, the charge-transfer gap gradually decreases [31]. Above a critical doping level  $p_{cr}$ , the charge-transfer gap becomes small enough to lead to the formation of a single band, similar to that predicted from the calculation of local density approximation. In this doping regime, both the polaronic oxygen holes and normal-state pseudogap disappear and a conventional Fermi-liquid state is restored. For LSCO,  $p_{cr}$  is larger than 0.24 while  $p_{cr} \simeq 0.19$  for YBCO [16]. In the intermediate region ( $0.10 < p < p_{cr}$ ), there coexist polaronic/bipolaronic oxygen holes and Fermi-liquid carriers [17] and the interaction between the two types of carriers leads to non-Fermi-liquid behavior. The Bose-Einstein condensation of local oxygen-hole pairs leads to  $d$ -wave order-parameter (OP) symmetry [32] in the underdoped region, consistent with some phase-sensitive experiments [33] which probe a  $d$ -wave OP symmetry of underdoped surfaces and/or interfaces [34, 35].

In summary, we have studied the oxygen-isotope effect on the superconducting transition temperature  $T_c$  in overdoped  $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$  with  $x = 0.10, 0.20$ , and  $0.25$ . We find that the oxygen-isotope exponent  $\alpha_O$  is small ( $\sim 0.02$ ) for  $x = 0.10$  and becomes substantial ( $\sim 0.1$ ) for  $x = 0.20$  and  $0.25$ . The doping level above which  $\alpha_O$  increases sharply coincides with the quantum critical point where the normal-state pseudogap starts to diminish. We further show that a combined mechanism based on strong coupling to multiple phonon modes and significant coupling to high-energy (1.6-2.0 eV) charge fluctuations is in quantitative agreement with the oxygen-isotope exponent and magnetic penetration depth above the quantum critical point [28] as well as with thermal-difference reflectance data [30].

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